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Thermal Degradation of Cereal Straws in Air and Nitrogen

A. E. GHALY* AND A. ERGUDENLER

Agricultural Engineering Department, Technical University of Nova Scotia, PO Box 1000, Halifax, Nova Scotia, Canada B3J 2X4

ABSTRACT

The termogravimetric behavior of four cereal straws (wheat, barley, oats, and rye) was examined at three heating rates (10, 20, and 50 °C/min) in air and nitrogen atmospheres. The thermal degradation rate in active and passive pyrolysis zones, the initial degradation temperature, and the residual weight at 600 °C were determined for these straws in both atmospheres. Increasing the heating rate increased the thermal degradation rate, and decreased both the initial degradation temperature and the residual weight at 600 °C. The higher the cellulosic content of the straw, the higher the thermal degradation rate and the initial degradation temperature. Also, higher ash content in the straw resulted in higher residual weight at 600 °C. The thermal degradation rate in active pyrolysis zone was lower in air atmosphere than in nitrogen atmosphere, whereas the thermal degradation rate in passive pyrolysis zone and the residual weight at 600 °C were higher in nitrogen atmosphere than in air atmosphere.

Index Entries: Cereal straw; thermal degradation; air; nitrogen; temperature.

INTRODUCTION

Agricultural biomass, as a renewable energy source, has attracted considerable attention during the past decade. As a result, numerous feasibility studies have been conducted to assess the potential of crop residues, specially cereal straw, for energy recovery through thermochemical conversion processes (*1-3*). Attempts have also been made to

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*Author to whom all correspondence and reprint requests should be addressed.

develop suitable systems for the recovery of energy from straw (*1,4*). Many of these projects could, however, achieve only limited success, owing mainly to the lack of adequate information on the straw properties pertaining to thermochemical conversion processes, as well as the lack of suitable preconversion processing systems. Thermochemical conversion technologies, such as combustion, gasification, and pyrolysis, use elevated temperatures to convert the energy content of biofuel materials. During thermochemical conversion, the thermal degradation of the various components of the organic fuel materials occurs. Full understanding of the biofuel properties and its thermochemical behavior is, thus, very essential for the proper design of thermochemical conversion systems (*5,6*).

Cellulose, hemicellulose, and lignin are the major components of straw. Cellulose is a remarkable pure organic substance, consisting solely of units of glucose held together in a giant straight chain molecule. The packing of the chains gives cellulose a so-called micelle structure, and imparts to the molecule its stable fibrous form. Cellulose is insoluble in most solvents, and in its native state, and has a low accessibility to acid and enzymatic hydrolysis (*7*). Hemicelluloses (arabinoglycuronoxylan and galactoglucomannans) are related to plant gums in composition, and occur in much shorter molecule chains than cellulose. They are derived mainly from chains of pentose sugars, and act as the cement material holding together the cellulose micells and fibers. Hemicelluloses are largely soluble in alkali and, as such, are more easily hydrolysed (*8*). Lignins are polymers of aromatic compounds. Their functions are to provide structural strength, provide sealing of water conducting system that links roots with leaves, and protect plants against degradation (*9*).

Although cellulose, one of the major constituents of straws, has been extensively investigated for its thermal behavior, straw itself has not been given the same consideration (*10*). Different components of straw exhibit different thermal behavior, with hemicellulose being the least stable component of straw. Shafizadeh (*11*) reported that cellulose and hemicellulose components of biomass breakdown at temperatures above 300°C, producing tarry products and relatively small amounts of pyrolyzates. However, the overall thermal behavior of the aggregate reflects the sum of the thermal behaviors of its components.

Thermal decomposition of biomaterials could take place in both anaerobic conditions (steam, hydrogen, and self-generated gas) and aerobic conditions (air and oxygen). Pyrolytic reactions cause incomplete thermal degradation of carbonaceous materials, resulting in char, condensible liquids, or tars and gaseous products, generally under anaerobic conditions (*12*). Gasification reaction occur as a combination of pyrolytic reactions, followed by higher temperature reactions of char, tars, and primary gases to yield mainly low mol wt gaseous products (*13*). Shafizadeh and DeGroot (*14*) and Lipska-Quinn et al. (*10*) reported a higher rate of thermal decomposition by oxidation of the substance at lower temperatures in presence of air (or oxygen) than in the absence of air (or oxygen).

The presence of inorganic materials, either as additives or natural ash content, strongly affects the thermal behavior of the cellulosic materials. The influence of the inorganic materials was first investigated primarily in relation to the problems of flame proofing and fire prevention (*15,16*). It has also been studied in connection with thermochemical conversion of biomass to fuel and chemicals (*14,17–19*). The catalytic effect of the inorganic materials is particularly pronounced with alkaline compounds and acidic reagents. Shafizadeh and DeGroot (*14*) studied the suppressive effect of diammonium phosphate, $(NH_4)_2PO_4$, on thermal behavior of cellulose. Lowered pyrolysis rate and increased char formation were observed by the authors. Fung and Graham (*17*) reported increased gasification rate and product yield when using potassium carbonate and calcium oxide. Nassar et al. (*19*) reported reduced flammable tars, volatiles and gases, and increased char when using flame-retardant inorganic chemicals.

The natural impurities and ash content could also produce profound effects. Straws from different cereal crops have widely varying ash contents and ash composition (*6*). Thus, the thermal analysis methods could indicate the effects of different straw compositions, ash contents, and ash compositions on lowering of the decomposition temperatures, the relative amounts of char and volatiles formed, the related heat of evaporation, and the heat of combustion of gaseous products.

Thermogravimetric analysis (TGA) is one of the major thermal analysis techniques used to study the thermal behavior of carbonaceous materials. The rate of weight loss of the sample as a function of temperature and time is measured to predict thermal behavior of the material. TGA provides a semiquantitative understanding of thermal degradation processes occurring during thermochemical conversion (*13*). Shafizadeh and DeGroot (*14*) reported that the chemical composition, heating rate, ambient atmosphere, temperature, and inorganic substances are the major factors that affect the thermal behavior of biomass.

OBJECTIVES

The aim of this study is to analyze the kinetics of thermochemical conversion of four common straws on the basis of their thermal degradation behavior. The specific objectives of the study were

1. To conduct thermogravimetric analysis on four cereal straws (wheat, barley, oats, and rye) at three heating rates (10, 20, and 50°C/min) in air (21% air and 79% nitrogen) and nitrogen; and

2. To determine the thermal degradation rate in active and passive pyrolysis zones, the initial degradation temperature, and the residual weight at 600°C for these straws in both atmospheres.

EXPERIMENTAL PROCEDURE

Straw Collection

Four major cereal crops were selected for the thermogravimetric analysis. These were: wheat, barley, oats, and rye. The most commonly grown variety in Nova Scotia of each crop was selected for the study. The selected varieties were: Max, Kadeth, Sentinel, and Kustro for wheat, barley, oats, and rye, respectively. Straw samples were obtained from harvested fields in the Annapolis Valley, Nova Scotia. Samples of approx 5 kg of straw were collected from each field shortly after harvest, placed in polyethylene bags, and transported to the Thermal Analysis Laboratory at the Technical University of Nova Scotia in Halifax. The straws were dried in an air-forced oven at 105°C on the same day to avoid deterioration caused by higher moisture content. The dried straws were then stored in polyethylene bags for future processing.

Sample Preparation

Dried straw samples of 1 kg each were first coarse-ground through a 20-mesh sieve on a medium size Wiley Mill. The coarse-ground materials were then reground through a 40-mesh sieve on the Wiley Mill in order to narrow the range of the particle size, and thus, obtain homogenous samples. The samples were dried at 105°C for 24 h in a forced air drying oven. These were stored in airtight plastic containers until they were needed for the thermogravimetric analysis. This procedure ensured reproducible thermogravimetric results.

Thermal Analysis

Straw samples were subjected to thermogravimetric analysis in two atmospheres (dry air and nitrogen) at three different heating rates. The heating rates used were: 10°C/min, 20°C/min, and 50°C/min. Samples weighing approx 80 mg were heated at preselected heating rates from ambient to 700°C in a NETZSCH Simultaneous Thermal Analyzer (STA 409). The accuracy of the system is 0.01 mg. The continuous record of weight loss and temperature was obtained. The data were analyzed to determine the following thermogravimetric analysis indices: thermal degradation rates in active and passive zones, initial degradation temperature, and residual weight at 600°C.

RESULTS AND DISCUSSION

The thermogravimetric behavior of the four types of straw at different heating rates (10, 20, and 50°C/min) in air and nitrogen atmospheres is shown in thermograms on Figs. 1–4. The results of kinetic parameters obtained from the analysis are presented in Tables 1 and 2 and shown in Figs. 5–8. Because the fine ground straw were powder-like, homogenous material, the results of the thermogravimetric analysis (TGA) were reproducible within ±0.01% by weight. The chemical composition and ultimate analysis of the straws are presented in Tables 3 and 4.

Thermal Degradation Rate

During thermal degradation of straws, two distinct pyrolysis zones were observed. Once the threshold temperature for thermal decomposition of the sample material was reached, there was a sharp drop in the weight of the sample, up to a certain temperature. This was termed active pyrolysis zone. Thereafter, the rate of weight loss decreased till it became zero. However, the present study was restricted to a maximum final temperature of 700°C. Thus, the passive pyrolysis zone was the one in which there was a decreasing rate of weight loss with respect to temperature. These two zones are quite evident in all thermograms shown in Figs. 1–4.

The thermal degradation rate (%/min), in both active and passive pyrolysis zones, increased with increases in heating rate for all straw samples in air and nitrogen atmospheres, as shown in Figs. 5 and 6. The proportional increase of thermal degradation rate with increases in heating rate was more in the active pyrolysis zone than in the passive pyrolysis zone for all samples, and in both atmospheres. Lipska-Quinn et al. (*10*) studied thermal decomposition of rice straw at different heating rates and found that the rate of degradation in the active pyrolysis zone markedly increased with the increase in heating rate.

The thermal degradation rate in the active pyrolysis zone was higher in nitrogen atmosphere for all the samples at all heating rates than in air atmosphere. However, it was observed to be lower in the passive pyrolysis zone. At 50°C/min heating rate, the thermal degradation of rye straw is the largest in air atmosphere, whereas barley straw is the largest in nitrogen atmosphere. This indicated that barley straw is more easily thermochemically degradable in an inert atmosphere, whereas rye is more easily thermochemically degradable in air.

The thermal degradability is affected by the chemical composition of straw as different components of lignocellulosic materials have different thermal behaviors. The higher thermal degradation rate of barley straw might be as a result of larger percentages of cellulose and hemicellulose components in comparison to those of wheat, barley, and oats, as shown

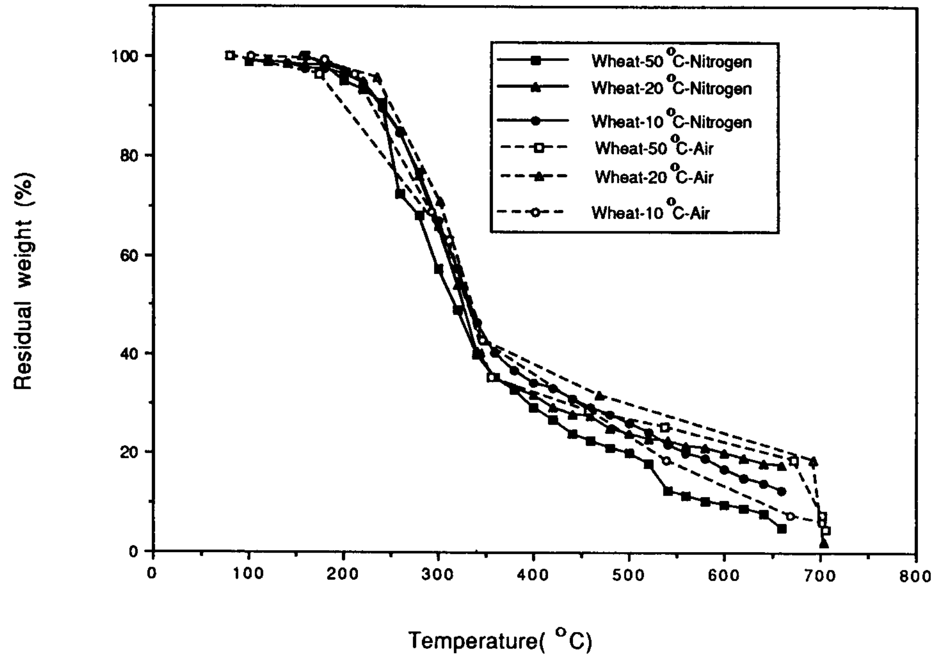

Fig. 1. Thermograms of wheat straw heated in air and nitrogen atmospheres at different heating rates.

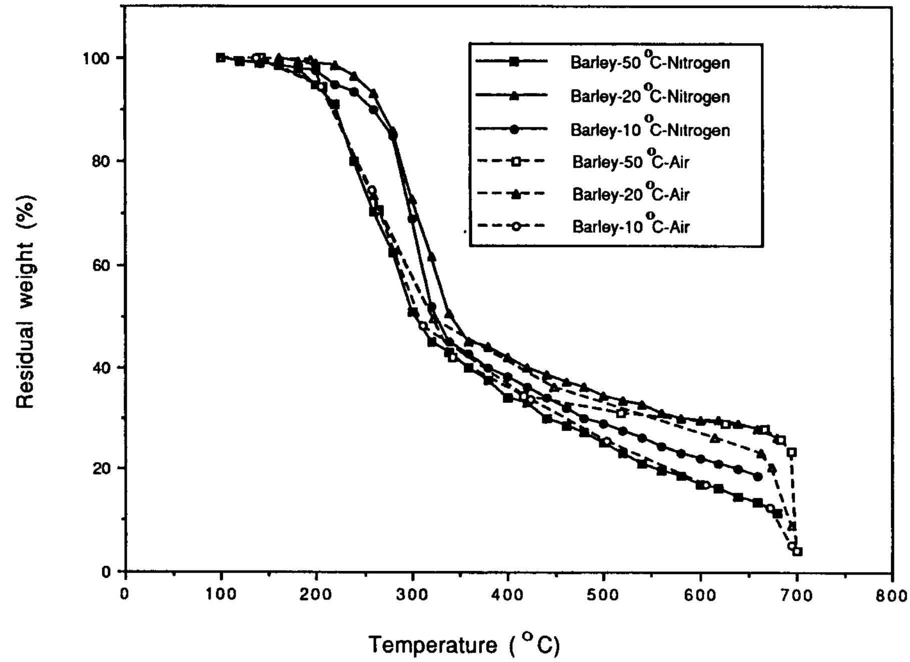

Fig. 2. Thermograms of barley straw heated in air and nitrogen atmospheres at different heating rates.

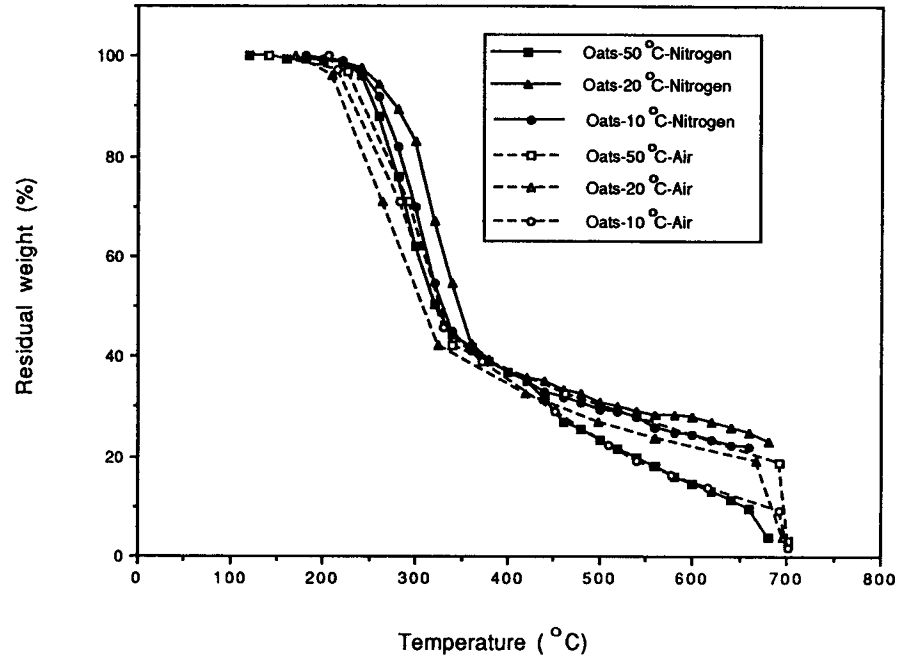

Fig. 3. Thermograms of oats straw heated in air and nitrogen atmospheres at different heating rates.

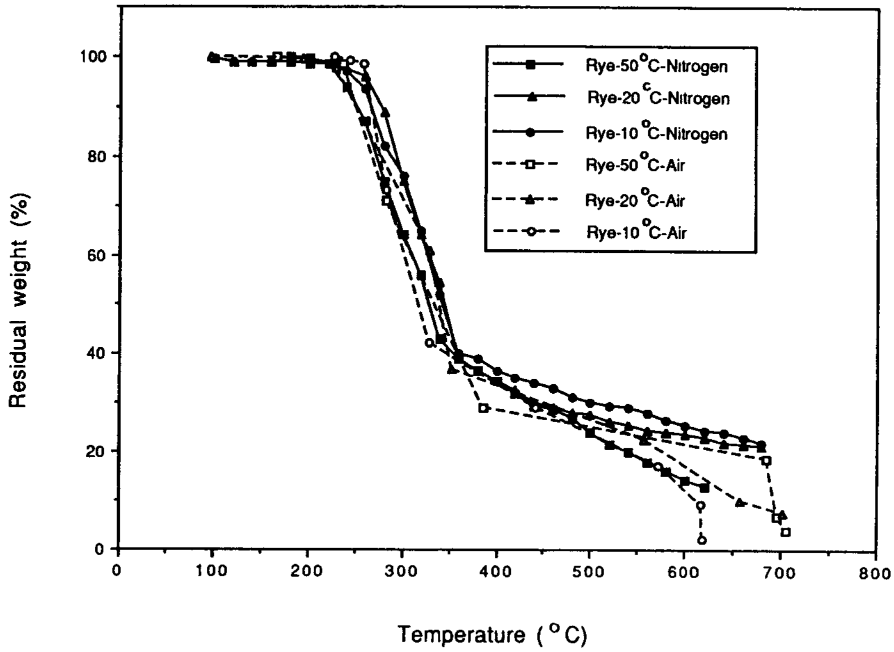

Fig. 4. Thermograms of rye straw heated in air and nitrogen atmospheres at different heating rates.

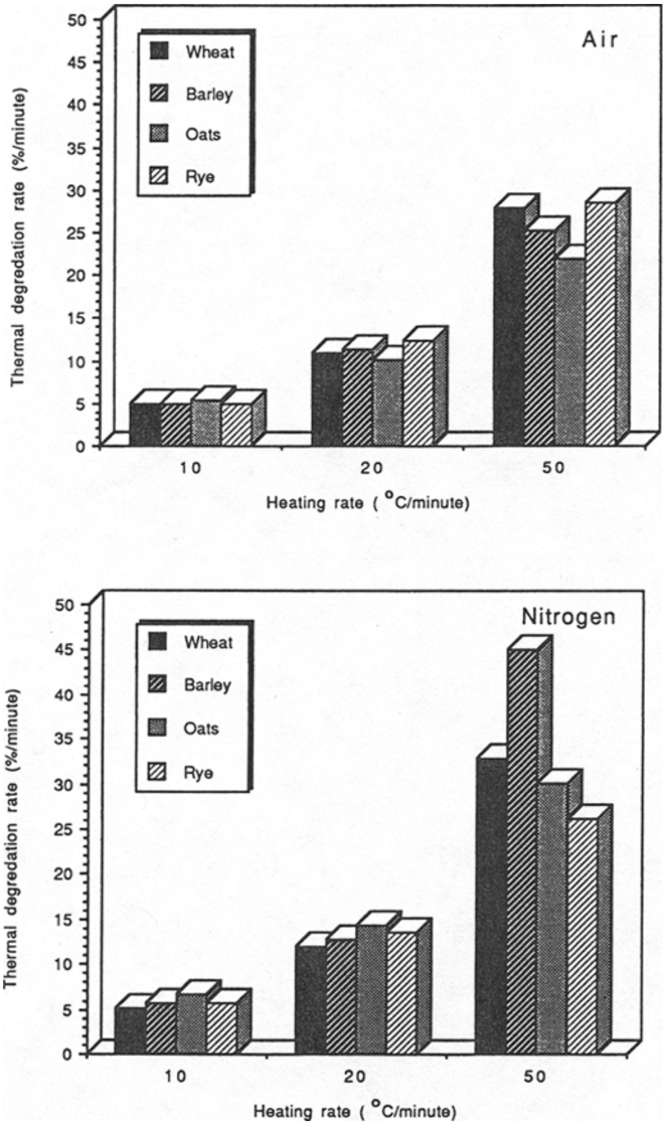

Fig. 5. Thermal degradation rate in active zone.

in Table 3. Similar results were obtained by Theander and Aman (*20*). Larger percentages of volatile matter and lower ash contents of rye straw, as compared to those of wheat straw (Table 4), might have also contributed the higher thermal degradability of rye straw. These results are in close agreement with those reported by Lipska-Quinn et al. (*10*) for rice straw.

Thermochemical degradation of the biofuel materials depends on the rate and extent of the pyrolytic reactions and the sequence of these reactions. Pyrolytic reactions, in turn, depend on the duration and intensity of heating of the substrate. Thus, different heating rates produce different end products. Shafizadeh and DeGroot (*14*) reported that long heat-

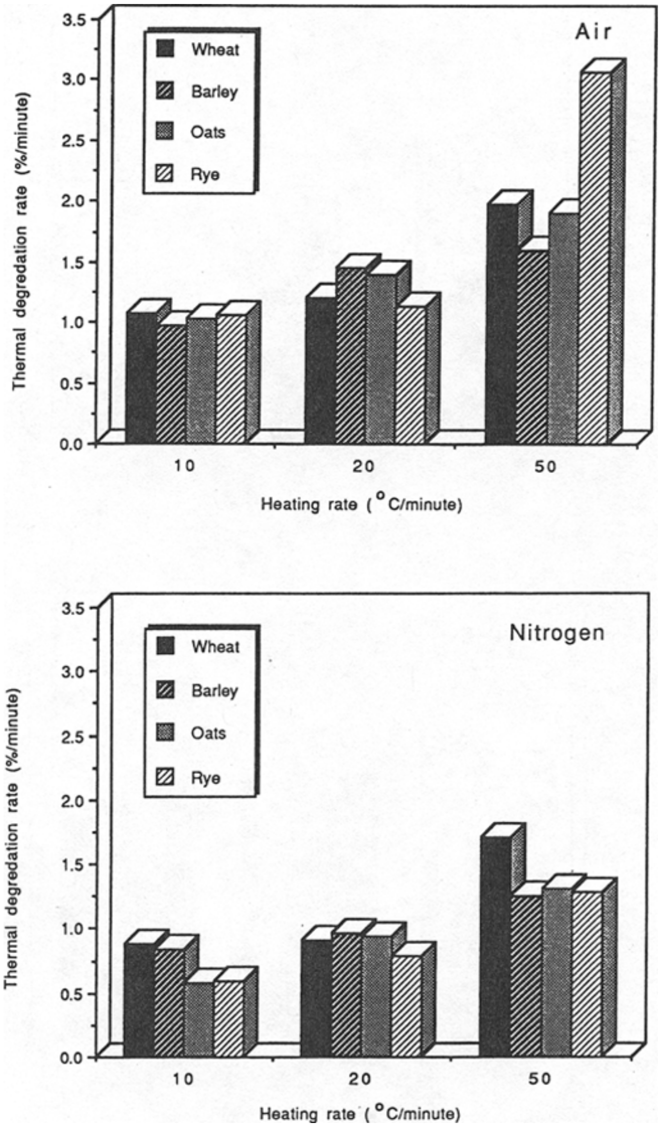

Fig. 6. Thermal degradation rate in passive zone.

ing periods (low heating rates) allow the sequence of consecutive reactions to take place. On the contrary, the flash pyrolysis (high heating rates) could reduce the secondary reactions and disallow the further degradation of the products.

Initial Degradation Temperature

The temperature at which the degradation starts is termed initial degradation temperature. The initial degradation temperature for rye straw,

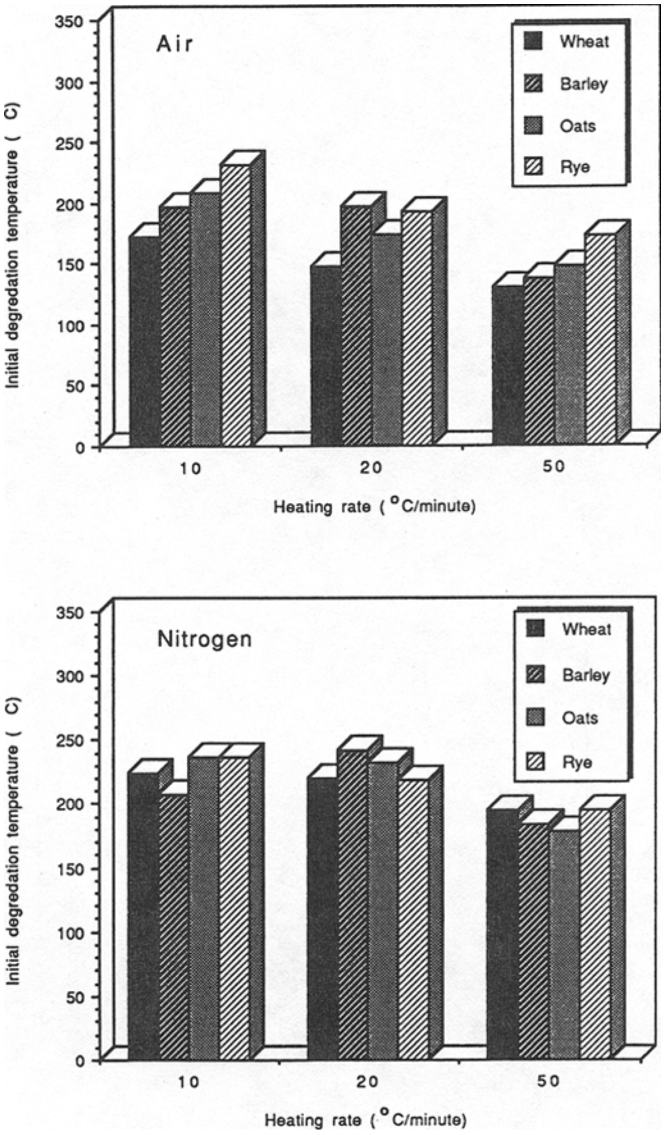

Fig. 7. Initial degradation temperature.

which apparently had the highest thermal degradation in air atmosphere, was the highest among the different straws at all thermal degradation rates in air atmosphere, except at 20°C/min, where barley and rye straws behaved similarly. With increases in heating rate, the initial degradation temperature decreased for all straw samples, with the exception of barley straw in nitrogen at 20°C/min. Wheat straw sample started degrading in air at 130°C while heated at 50°C/min, whereas at 10°C/min heating rate, its initial degradation temperature was 172°C. Rye straw started degrading at 231°C, 193°C, and 172°C when heated at 10°C/min, 20°C/min, and 50°C/min, respectively. The initial degradation temperature for all straw

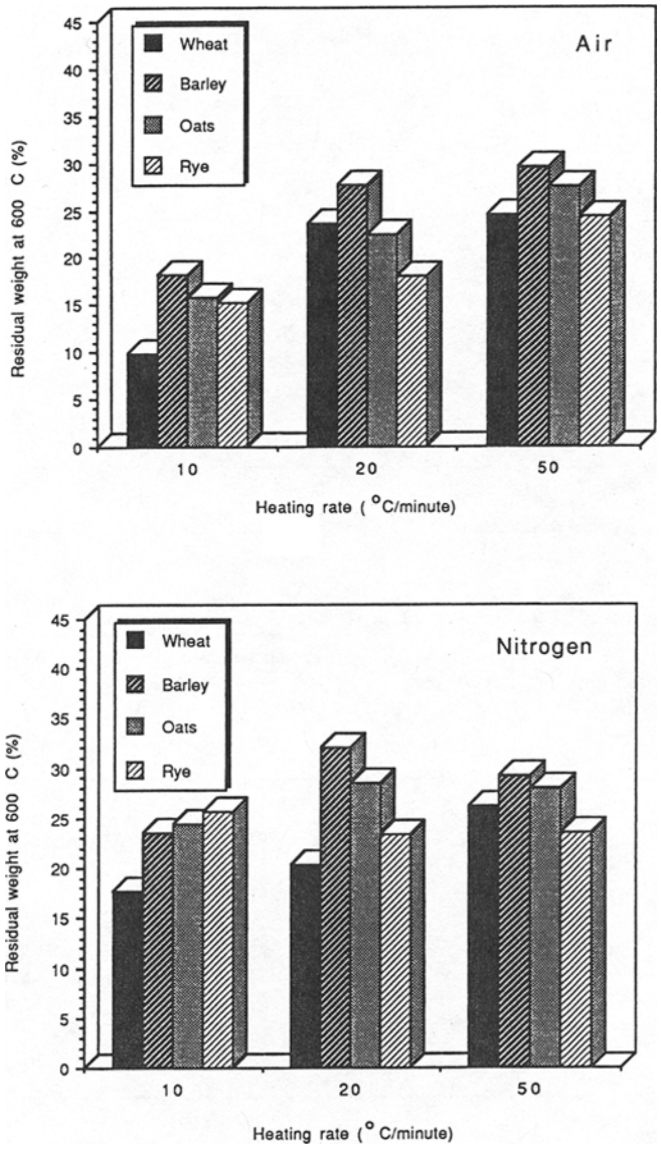

Fig. 8. Residual weight at 600°C.

samples at all heating rates was higher in nitrogen atmosphere than in air atmosphere.

Lipska-Quinn et al.(*10*) observed marked decrease in initial degradation temperature for rice straw and its components while increasing heating rate. Hemicellulose and lignin components of lignocellulosic material start degrading at lower temperatures than cellulose. Their rate of thermal degradation is lower than that of cellulose, as observed by Shafizadeh and McGinnis (*21*). Thus, the higher percentage of cellulose in rye straw as compared to that in wheat straw, might have caused the higher initial degradation temperature for rye, as reported by Theander and Aman (*20*).

Table 1
Thermogravimetric Analysis of Straw In Air Atmosphere

Straw	Heating Rate (°C/min)	Thermal Degradation Rate (%/min) Active Zone	Passive Zone	Initial Degradation Temperature (°C)	Residual Weight at 600°C (%)
Wheat	10	5.06	1.08	172	9.90
	20	11.04	1.20	147	23.64
	50	27.87	1.98	130	24.54
Barley	10	5.01	0.98	196	18.18
	20	11.46	1.45	196	27.64
	50	25.21	1.60	137	29.64
Oats	10	5.46	1.03	208	15.84
	20	10.12	1.40	174	22.49
	50	21.94	1.90	147	27.60
Rye	10	5.06	1.06	231	15.27
	20	12.31	1.13	193	18.02
	50	28.59	3.07	172	24.27

The sample size was 80 mg
The accuracy of the balance was 0.01 mg (0.01% of the sample weight)

Table 2
Results of Thermogravimetric Analysis of Straws In Nitrogen Atmosphere

Straw	Heating Rate (°C/min)	Thermal Degradation Rate (%/min) Active zone	Passive zone	Initial Degradation Temperature (°C)	Residual Weight at 600$_0$C (%)
Wheat	10	5.12	0.88	224.0	17.77
	20	12.04	0.91	219.5	20.83
	50	32.86	1.71	195.0	26.27
Barley	10	5.73	0.84	207.2	23.58
	20	12.80	0.97	242.0	32.00
	50	45.11	1.26	184.0	29.25
Oats	10	6.65	0.58	236.5	24.48
	20	14.43	0.94	233.0	28.46
	50	30.15	1.31	178.2	27.97
Rye	10	5.72	0.59	236.5	25.67
	20	13.66	0.78	219.0	23.46
	50	26.12	1.28	195.5	23.53

Residual Weight at 600 °C

Shafizadeh and DeGroot (*14*) reported that the three major constituents of lignocellulosic materials (hemicellulose, cellulose, and lignin) are chemically reactive, and decompose thermochemically in the temperature range of 150–500 °C (hemicellulose occurs at 150–350 °C, cellulose occurs at 275–350 °C, and Lignin occurs at 250–500 °C). Thus, a temperature level higher than 500 °C (i.e., 600 °C) was selected to compare the residual weights of different straw samples under study.

Barley straw exhibited the largest weight at 600 °C, in comparison to the other three straws, as shown in Fig. 8. This might be related to the

Table 3
Chemical Composition of Straw

Crop	Chemical Composition (% on dry weight basis)		
	Cellulose	Hemicellulose	Lignin
Wheat	27	21	21
Barley	31	25	22
Oats	30	22	23
Rye	30	23	20

Values are the average of 3 replicates.
Coefficient of variability is less than 0.30%

Table 4
Proximate Analysis of Straw

Straw	Proximate Analysis (% dry basis)		
	Volatile Matter	Fixed Carbon	Ash
Wheat	79.61	16.76	3.63
Barley	73.84	18.84	7.32
Oats	78.88	17.04	4.08
Rye	83.02	15.01	1.97

Values are the average of 3 replicates.
Coefficient of variability is less than 0.30%

larger ash content of barley straw, as compared to that of other straws (Table 4). Residual weight increased with increase in heating rate with all samples in air atmosphere, as well as in nitrogen atmosphere. Lipska-Quinn et al. (*10*) also observed increases in residual weight with increase in heating rate during the thermal degradation of rice straw in air. This indicated that sufficient time was not available for the consecutive pyrolytic reactions to occur at higher heating rates. Thus, larger percentages of samples were left unconverted at higher heating rates. A higher residual weight was observed in nitrogen atmosphere than in air atmosphere for all samples at all heating rates. Similar results were reported for rice straw by Lipaka-Quinn at al. (*10*).

The industrial processes for biomass gasification and liquefaction are usually designed for temperatures above 600°C. The higher temperatures are required to convert the char, at appreciable conversion rates, through heterogenous reactions to gaseous components, such as water, carbon dioxide, and oxygen. Shafizadeh and DeGroot (*14*) reported that at higher temperatures, presence of water and steam speeds up the breakdown and degradation of the molecules by hydrolysis of the substrate and rearrangement of intermediate products. The steam plays a more important and direct role as a reactant in the gasification of char and related processes. At higher temperatures, carbon dioxide and hydrogen also act as reactants. In the presence of air or oxygen, at higher temperatures, the oxidation of the volatile pyrolysis products results in flaming combustion. This further enhances the oxidation of char.

CONCLUSIONS

1. During thermal decomposition of straw, the thermal degradation rate increased as the heating rate was increased in both air and nitrogen atmospheres.
2. The higher the cellulosic content of the straw, the higher its thermal degradation rate. Rye straw has higher thermal degradation rate in air atmosphere than those of wheat, barley, and oats, mainly owing to higher cellulosic content.
3. Initial degradation temperature of straw decreased as the heating rate was increased.
4. The initial degradation temperature was higher for all straw samples in nitrogen atmosphere than in air atmosphere.
5. The lower the cellulosic content of the straw, the lower is its initial degradation temperature. Wheat straw has the lowest initial degration temperature among the four straws under study, mainly because of lower cellulosic content.
6. The thermal degradation rate in active pyrolysis zone was lower in air atmosphere than in nitrogen atmosphere, whereas that in passive zone was higher in air atmosphere than in nitrogen atmosphere for all samples.
7. Residual weight at 600 °C increased as the heating rate was increased in both atmospheres for all samples, indicating incomplete conversion resulting from insufficient time for pyrolytic reactions to take place.
8. The higher the ash content of the straw, the larger is the residual weight. Barley straw has higher residual weight (at 600 °C) than other straw because of its higher ash content.
9. Rye straw is highly degradable through thermochemical conversion processes in comparison to wheat straw, barley straw, and oats straw.

10. The residual weight at 600°C was higher in nitrogen atmosphere than in air temperature for all straw samples.

REFERENCES

1. Peil, J. E. (1980), Evaluation of a system utilizing biomass (straw) as a fuel for crop drying and heating on a farm. Proceedings of the Second Canadian Bioenergy R & D Seminar, National Research Council of Canada, Ottawa, Ontario, pp. 11-16.
2. Colwell, H. T. M. (1983), The potential for a sustained energy for combustible crop residues in the Canadian Agriculture and Food System: A National Assessment. Technical Report, Energy Analysis and Policy Division, Agriculture Canada, Ottawa, Ontario.
3. Nemetz, I. (1983), Economics of crop residue gasification system: Economic analysis and research priorities. Technical Report, Energy Analysis and Policy Division, Agriculture Canada, Ottawa, Canada.
4. Strehler, A. (1982), Technology of heat and power production from solid fuel. Proceedings of the International Conference on Energy From Biomass (Strub, A., P. Chartier, and G. Schleser, eds.). Applied Science Publishers, Barking, Essex, pp. 346-358.
5. Ebling, J. M. and Jenkins, B. M. (1985), *Trans. ASAE* **28(3),** 898-902.
6. Ghaly, A. E., Al-Taweel, A. M., Hamdullaphur, F., and Ergudenler, A. (1989). Thermogravimetric characteristics of straws. Proceedings of the Seventh Canadian Bioenergy R & D Seminar, National Research Council of Canada, Ottawa, Ontario, pp. 647-654.
7. Stacey, M. (1976), *Agri. Progress* **51,** 69-78.
8. Theander, O. (1985), In *Fundamentals of Thermochemical Biomass Conversion,* Overend, R. P., Mile, T. A., and Mudge, L. K., eds., Elsevier, New York, pp. 35-60.
9. Glasser, W. G. (1985), In *Fundamentals of Thermochemical Biomass Conversion,* Overend, R. P., Mile, T. A., and Mudge, L. K., eds., Elsevier, New York, pp. 61-76.
10. Lipska-Quinn, A. E., Zeronian, S. H., and McGee, K. M. (1985), In *Fundamentals of Thermochemical Biomass Conversion,* Overend, R. P., Mile, T. A., and Mudge, K. K., eds., Elsevier, New York, pp. 453-471.
11. Shafizadeh, F. (1968). Pyrolysis and combustion of cellulosic materials. *Adv. Carbohydrate Chem.* **23,** 419.
12. Soltes, E. J. and Elder, T. J. (1981), In *Organic Chemical from Biomass,* Goldstain, I. S., ed., CRC Press, Boca Raton, Florida, pp. 63-99.
13. Milne, T. (1981), In *Biomass Gasification Principles and Technology,* Noyes Data Corporation, Park Ridge, New Jersey, pp. 91-118.
14. Shafizadeh, F. and DeGroot, W. F. (1976), In *Thermal Uses and Properties of Carbohydrates and Lignins,* Academic, New York, pp. 1-6.
15. MacKay, G. D. M. (1968), Effect of inorganic salts on the pyrolysis of cellulose. *Forest Products* **18,** 71.
16. Broido, A. (1966), *Pyrodynamics* **4,** 243.

17. Fung, D. P. C. and Graham, R. (1979), The role of catalysis in wood gasification. Paper presented at the 198th Meeting of the American Chemical Engineering Society, Washington, D.C.
18. Hallen, R. T., Sealock, L. J., and Cuello, R. (1985), In *Fundamentals of Thermochemical Biomass Conversion,* Overend, R. P., Mile, T. A., and Mudge, L. K., eds., Elsevier, New York, plp. 157-166.
19. Nassar, M. M., Bilgesy, A., and MacKay, G. D. M. (1986), *Wood and Fiber Science* **18(1),** 3-10.
20. Theander, O. and Aman, P. (1978), *Swedish J. Agric. Res.* **8,** 189-194.
21. Shafizadeh, F. and McGinnis, G. D. (1970), *Carbohydrate Res.* **16,** 273-282.